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INTERACTION OF REFRACTORY COMPOUNDS WITH MOLTEN METALS

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The interaction of refractory compounds such as carbides, borides, nitrides, and silicides in contact with molten metals (Cu, Mg, Fe, Co, Ni, Si, Cd, Zr, etc.) is discussed and tabulated for four groups, classified by degree of interaction. TiN, ZrN, BN, and ZrB_2 showed no interaction, making them suitable for prolonged contact.

Author

The improvement, supervision and automation of many processes in metallurgy, chemical engineering, electric power and other industries require fire-resistant materials that also withstand the action of molten metals at high temperatures. The physicochemical and thermodynamic properties of oxide refractories are such that in many cases they cannot meet the requirements of the new technology.

Refractory compounds - carbides, borides, nitrides, and silicides of certain transition metals and compounds of combinations of nitrogen, carbon, silicon and boron - are promising refractory materials.

The melting points of such materials generally are above 2000-3000° C, and they are chemically highly resistant to acids, alkalies, and fused salts (Bibl.1).

However, the resistance of refractory compounds in contact with molten metals has been little studied. The available data indicate that many carbides,

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** Numbers in the margin indicate pagination in the original foreign text.

borides, nitrides, and silicides resist the action of chemically active molten metals.

Various authors occasionally report different results for materials of the same type, since the experiments were run under different thermodynamic conditions on materials of varying chemical purity, etc.

The Institute of Cermets and Special Alloys, Academy of Sciences Ukrainian SSR, has studied the interaction of the carbides and borides of titanium, zirconium, chromium, molybdenum, and tungsten, as well as the nitrides of titanium, zirconium, boron, and silicon, and the disilicide of molybdenum (whose chemical composition is given in Table 1) with molten copper, magnesium, zinc, cadmium, aluminum, silicon, titanium, zirconium, tin, lead, vanadium, bismuth, chromium, manganese, iron, cobalt and nickel all of which were above 99% pure.

The refractory compounds were contacted with the molten metals by melting the metal in a crucible made of the test material, in a vacuum furnace under a residual pressure of 10^{-2} mm Hg or in a protective atmosphere. The crucibles /21 were made from the powdered refractory compound by hot-pressing, or by pressing blanks followed by oxidation. Table 2 shows the results.

To find the relative activity of the interaction between the contacted pairs of materials, the molten metal, at its fusion point, was kept 5 min in the crucible (Cd, Zn, Sn, Pb, Bi, and Al were heated above the melting point, to 400° C), and then cooled within 20-30 min to room temperature. Polished sections for metallographic study were then prepared from the button of metal (alloy) and from the crucible walls.

If brief contact failed to give a distinct interaction, the molten metals were kept in the crucibles for 1, 2, 5, 10, 40, 80 or 100 hrs, or longer under laboratory conditions and, in some cases, under industrial conditions.

TABLE 1

CHEMICAL COMPOSITION OF REFRACTORY COMPOUNDS STUDIED IN CONTACT WITH MOLTEN METALS

Compound	Content, Wt. %					
	Me	C_{bound}	C_{free}	B	N	Si
TiC	80.88	18.50	0.22	—	—	—
ZrC	88.20	11.39	0.68	—	—	—
Cr_3C_2	85.80	12.44	0.06	—	—	—
Mo_2C	93.90	5.88	0.10	—	—	—
WC	93.80	5.98	0.10	—	—	—
TiB	68.80	—	0.30*	30.2	—	—
ZrB_2	79.95	—	0.20*	19.1	—	—
CrB_2	68.92	—	0.20*	28.55	—	—
Mo_2B_5	86.90	—	—	11.7	—	—
W_2B_5	88.00	—	—	12.9	—	—
TiN	78.1—82.0	—	—	—	18.0—21.9	—
ZrN	86.68	—	—	—	13.32	—
BN	—	—	—	42.88	55.20	—
Si_3N_4	—	—	—	—	39.50	59.50
$MoSi_2$	62.51	—	—	—	—	36.50

* Total carbon content

After prolonged contact, the specimens of refractory compounds and metals were subjected to chemical, spectral, and X-ray analysis to determine their content of elements from the contact material.

Metallographic structural studies were also run on all specimens, together with determinations of the phase composition and the microhardness of the phases. The phases were determined and the conclusions as to the character of the interaction between the contact materials were substantiated from the variation in phase composition, the depth of penetration of the new phases, the structure of the crucible-wall material or metal-button material, the principal direction of migration of the interacting masses, and from the microhardness of the phases constituting the structure, giving due consideration to the thermodynamic characteristics.

The changes in state of the materials as a result of their interaction

were evaluated on a five-point scale. The degree of change was based on the quantitative and qualitative indices obtained by analysis of the MeX-Me specimens after their contact.

In determining the degree of activity of the interaction we considered the duration of contact, the degree of superheat of the molten metal [expressed by the ratio of the temperature differences (boiling point - melting point) to (experimental temperature - melting point)], and the concentration of the elements of the refractory compound in the molten metal or in the metal being smelted (new phase with this particular metal as base) in the structure of the refractory compounds after their contact.

The pairs of materials studied can be classified into four groups by /23 activity of interaction, on the basis of the experimental results. The group showing no sign of interaction is characterized by point 1 on the scale of activity and can be recommended for direct use in cases of protracted contact.

The group of materials with point 2 on the scale of activity may be used for brief contacts where the purity of the metal need not be very high after melting. The interaction activity of materials of this group may be lowered by the incorporation of additives, and especially by preparing cermets with compounds of this group as base.

Examples are an alloy of titanium carbide with 20% cobalt resistant to aluminum bronze (Bibl.2), borolites (Bibl.3), alloys of boron with graphite (Bibl.4), alloys of silicon carbide with silicon nitride, and a number of others.

The use of refractory compounds with point 4 or 5 on the scale in the formulation of cermets resistant to contact with these metals is more complicated or altogether impossible. Pairs of these materials in themselves may

TABLE 2

CHARACTER OF INTERACTION OF REFRACTORY COMPOUNDS IN CONTACT WITH MOLTEN METALS *1

MeX \ Me	Mg, degrees (duration of contact 2 hrs at 800°C)	Cu			Zn (t=940° C)		Cd			Al (temp. 1000° C)		Si (temp. 1450° C)		Sn			Pb			Bi			Duration of contact, 5 min				
		degrees	minutes*	t*3	degrees	hours	degrees	hours	t	degrees	minutes	degrees	minutes	degrees	hours	t	degrees	hours	t	degrees	hours	t	V (t=1730° C)	Cr (t=1830° C)	Mn (t=1270° C)	Fe (t=1560° C)	Ni (t=1460° C)
TiC	2	2	300	1100	2	168	1	10	450	2	300	5	5	1	10	350	1	10	350	1	10	370	5	5	4	5	5
ZrC	2	2	120	1100	2	168	1	10	450	4	60	5	5	1	10	350	1	10	350	1	10	370	5	5	5	5	5
Cr_3C_2	5	5	60	1100	5	24	2	10	450	5	60	5	5	1	10	800	1	10	800	1	10	800	—	—	5	5	5
Mo_2C	4	4	60	1100	4	168	1	10	550	5	5	5	5	1	10	800	1	10	800	1	10	800	5	5	5	5	5
WC	4	4	60	1100	2	144	1	10	550	5	5	5	5	1	10	800	1	10	800	1	10	800	5	5	5	5	5
TiB_2	2	2	300	1100	1	240	1	80	550	1	30*	5	5	1	80	350	1	80	350	1	80	370	5	5	4	4	5
ZrB_2	1	1	300	1100	1	180	1	80	550	2	300	4	5	1	80	350	1	80	350	1	80	370	5	5	4	1	4
CrB_2	5	5	60	1100	1	132	2	80	550	4	300	5	5	1	80	350	1	80	350	1	80	370	5	5	5	5	5
Mo_2B_5	4	4	60	1100	1	168	1	10	450	5	5	5	5	1	10	800	1	10	800	1	10	800	5	5	5	5	5
W_2B_5	2	2	60	1100	1	168	1	10	450	5	5	5	5	1	10	800	1	10	800	1	10	800	5	5	5	4	5
TiN	1	2	60	1100	1	168	1	40	450	5	5	5	5	2	40	350	2	40	350	2	40	370	5	5	4	5	5
ZrN	1	2	60	1100	1	168	1	40	450	5	60	5	5	2	40	350	2	40	350	2	40	370	5	5	5	4**	5
BN	1	1	300	1100	1	168	1	10	550	2	60	1	120	1	10	800	1	10	800	1	10	800	5	5	5	4**	4
Si_3N_4	1	1	300*	1200	1	168	1	10	550	1	300*	4	5	1	10	800	1	10	800	1	10	800	5	5	5	5	5
$MoSi_2$	5	5	5	1100	1	204	1	80	450	5	5	5	5	1	80	350	1	80	350	1	80	370	5	5	5	5	5

* Hours

*1 On 5 min contact of MeX with Ti at 1460°C, with Zr at 1930°C and with Co at 1500°C: point 5 on the scale

*2 Duration of contact

*3 t = temperature of metal, °C

*4 Duration of contact, 1 hr

obviously be used as bases for cermets resistant to other molten metals.

BIBLIOGRAPHY

1. Samsonov, G.V.: Refractory Compounds (Tugoplavkiye soyedineniya). Metallurgical Press, Moscow, 1953.

2. Bochkov, F.V.: Ogneupory, No. 1, 1960.

3. - Iron Age, No. 173, p.133, 1954.

4. Samsonov, G.V. et al.: Ogneupory, No. 7, 1962.